CLAIMS

1. A composition comprising a solvent, a hetero-olefin, and a hydrogen-bond donor.

2. The composition of claim 1, wherein said composition does not comprise a metal.

3. The composition of claim 1, wherein said composition does not comprise a transition metal.

4. The composition of claim 1, wherein said composition does not comprise a Lewis acid.

5. A composition consisting essentially of a solvent, a hetero-olefin, a diene, and a hydrogen-bond donor.

6. The composition of claim 1 or 5, wherein said hetero-olefin is a dienophile.

7. The composition of claim 1 or 5, wherein said hetero-olefin has the structure X=Y, wherein X and Y are different atoms.

8. The composition of claim 7, wherein X is selected from the group consisting of $R^1{}_2C$, R^2N, O, and S; and

Y is selected from the group consisting of O, NR^2 , and S;

wherein R^1 are the same or independently selected from the group consisting of hydrogen, halogen, alkyl, alkene, alkyne, cycloalkyl, aromatic, heteroatom containing alkyl, and heteroatom containing aromatic; and

wherein R^2 is selected from the group consisting of hydrogen, halogen, alkyl, alkene, alkyne, cycloalkyl, aromatic, heteroatom containing alkyl, heteroatom containing cycloalkyl, and heteroatom containing aromatic.

9. The composition of claim 1 or 5, wherein said hetero-olefin comprises ketone functionality.

10. The composition of claim 1 or 5, wherein said hetero-olefin has an aldehyde functionality.

11. The composition of claim 1 or 5, wherein said hetero-olefin has an imine functionality.

12. The composition of claim 1 or 5, wherein said hetero-olefin has a thioketone functionality.

13. The composition of claim 1 or 5, wherein said hetero-olefin has a carboxylic acid functionality.

14. The composition of claim 1 or 5, wherein said hetero-olefin has a carboxylic ester functionality.

15. The composition of claim 1 or 5, wherein said hetero-olefin comprises a nitro-group.

16. The composition of claim 1 or 5, wherein said hetero-olefin comprises the structure X≡Y, wherein X and Y are different atoms.

17. The composition of claim 16, wherein X is R^1C and Y is N.

18. The composition of claim 1 or 5, wherein said hydrogen-bond donor comprises a stereogenic center and a hydrogen-heteroatom bond.

19. The composition of claim 18, wherein said hydrogen-heteroatom bond is between hydrogen and oxygen or between hydrogen and nitrogen.

20. The composition of claim 1 or 5, wherein said hydrogen-bond donor comprises a stereogenic center and is selected from the group consisting of alcohols, phenols, carboxylic acids, amides, amines, amino acids, and peptides.

21. The composition of claim 1 or 5, wherein said hydrogen-bond donor is a chiral alcohol.

22. The composition of claim 21 wherein said chiral alcohol is a diol.

23. The composition of claim 21 wherein said chiral alcohol is a 1,4-diol.

24. The composition of claim 21 wherein said chiral alcohol is a tartaric acid derivative.

25. The composition of claim 21, wherein said chiral alcohol is selected from the group consisting of TADDOL, 1-Napthyl-TADDOL, TADDOL derivatives, BINOL, BINOL derivatives, tartaric acid dialkyl ester derivatives, and hydrobenzoin derivatives.

26. The composition of claim 1, further comprising a diene.

27. The composition of claim 26, wherein said diene comprises a heteroatom.

28. The composition of claim 26, wherein said diene comprises the structure $C=C(R^3)-C=C-Z$, wherein R^3 and Z comprise heteroatoms.

29. The composition of claim 26 wherein said diene is a 1,3-butadiene, wherein said 1,3 butadiene is substituted with an electron donating group at a 1 position and an electron donating group at a 3 position.

30. The composition of claim 29 wherein said electron donating group at the 3 position comprises a protected alcohol.

31. The composition of claim 29 wherein said electron donating group at the 1 position comprises a substituted nitrogen.

32. A method comprising combining a hetero-olefin and a chiral hydrogen-bond with a solvent to form a solution for a time sufficient to allow an enantioselective reaction.

33. The method of claim 32, wherein said solution does not comprise a metal.

34. The method of claim 32, wherein said solution does not comprise a transition metal.

35. The method of claim 32, wherein said solution does not comprise a Lewis acid.

36. A method comprising forming a solution consisting essentially of a solvent, a hetero-olefin, a diene, and a chiral hydrogen-bond donor, wherein sufficient time is allowed for enantioselective reaction.

37. The method of claim 32 or 36, wherein said reaction is selected from the group consisting of Diels-Alder, dipolar cycloadditions, carbene addition, cyclopropanation, aziridination, nucleophilic substitution, nucleophilic addition to carbonyls, nucleophilic addition to alpha, beta unsaturated carbonyls, nucleophilic addition to imines, cyanohydrin formation, cyanoamine formation, and reductions.

38. The method of claim 32 or 36, wherein said reaction is a Diels-Alder type reaction.

39. The method of claim 32 or 36, wherein said reaction is a reduction.

40. The method of claim 32 or 36, wherein said reaction is a nucleophilic substitution.

41. The method of claim 32 or 36, wherein said enantioselective synthesis results in an enantiomeric excess of at least 60 %.

42. The method of claim 32 or 36, wherein said enantioselective synthesis results in an enantiomeric excess of at least 70 %.

43. The method of claim 32 or 36, wherein said enantioselective synthesis results in an enantiomeric excess of at least 80 %.

44. The method of claim 32 or 36, wherein said enantioselective synthesis results in an enantiomeric excess of at least 90 %.

45. The method of claim 32 or 36, wherein said enantioselective synthesis results in an enantiomeric excess of at least 95 %.

46. The method of claim 32 or 36, wherein said hetero-olefin is a dienophile.

47. The method of claim 32 or 36, wherein said hetero-olefin has the structure X=Y, wherein X and Y are different atoms.

48. The method of claim 47, wherein X is selected from the group consisting of $R^1{}_2C$, R^2N, O, and S; and

Y is selected from the group consisting of O, NR^2, and S;

wherein R^1 are the same or independently selected from the group consisting of hydrogen, halogen, alkyl, alkene, alkyne, cycloalkyl, aromatic, heteroatom containing alkyl, and heteroatom containing aromatic; and

wherein R^2 is selected from the group consisting of hydrogen, halogen, alkyl, alkene, alkyne, cycloalkyl, aromatic, heteroatom containing alkyl, heteroatom containing cycloalkyl, and heteroatom containing aromatic.

49. The method of claim 32 or 36, wherein said hetero-olefin has a ketone functionality.

50. The method of claim 32 or 36, wherein said hetero-olefin has an aldehyde functionality.

51. The method of claim 32 or 36, wherein said hetero-olefin has an imine functionality.

52. The method of claim 32 or 36, wherein said hetero-olefin has a thioketone functionality.

53. The method of claim 32 or 36, wherein said hetero-olefin has a carboxylic acid functionality.

54. The method of claim 32 or 36, wherein said hetero-olefin has a carboxylic ester functionality.

55. The method of claim 32 or 36, wherein said hetero-olefin comprises a nitro-group.

56. The method of claim 32 or 36, wherein said chiral hydrogen-bond donor comprises a stereogenic center and a hydrogen-heteroatom bond.

57. The method of claim 56, wherein said hydrogen-heteroatom bond is between hydrogen and oxygen or between hydrogen and nitrogen.

58. The method of claim 32 or 36, wherein said chiral hydrogen-bond donor comprises a stereogenic center and is selected from the group consisting of alcohols, phenols, carboxylic acid, carboxylic ester, amides, amines, amino acids, and peptides.

59. The method of claim 32 or 36, wherein said chiral hydrogen-bond donor is a chiral alcohol.

60. The method of claim 59 wherein said chiral alcohol is a diol.

61. The method of claim 59 wherein said chiral alcohol is a 1,4-diol.

62. The method of claim 59 wherein said chiral alcohol is a tartaric acid derivative.

63. The method of claim 59, wherein said chiral alcohol is selected from the group consisting of TADDOL, 1-Napthyl-TADDOL, TADDOL derivatives, BINOL derivatives, tartaric acid dialkyl ester derivatives, and hydrobenzoin derivatives.

64. The method of claim 32, further comprising a diene.

65. The method of claim 64, wherein said diene comprises a heteroatom.

66. The method of claim 64, wherein said diene comprises the structure $C=C(R^3)-C=C-Z$, wherein R^3 and Z comprise heteroatoms.

67. The method of claim 64 wherein said diene is a 1,3-butadiene, wherein said 1,3 butadiene is substituted with an electron donating group at a 3 position and an electron donating group at a 1 position.

68. The method of claim 67 wherein said electron donating group at the 3 position comprises a protected alcohol.

69. The method of claim 67 wherein said electron donating group at the 1 position comprises a substituted nitrogen.

70. A method of performing a cycloaddition reaction comprising:

combining a first reactant and a second reactant in a hydrogen bonding solvent to form a reaction mixture; and

reacting the first reactant and the second reactant to form a cycloadduct.

71. The invention of claim 70 wherein the reaction mixture is substantially free of metals.

72. The invention of claim 70 wherein the cycloaddition comprises a [4+2] cycloaddition.

73. The invention of claim 72 wherein the first reactant comprises a diene and the second reactant comprises a heterodienophile.

74. The invention of claim 73 wherein the heterodienophile comprises a ketone.

75. The invention of claim 74 wherein the ketone comprises a cyclic ketone.

76. The invention of claim 71 wherein the first reactant comprises a diene and the second reactant comprises a heterodienophile.

77. The invention of claim 72 wherein the first reactant comprises a diene and the second reactant comprises a dienophile.

78. The invention of claim 77 wherein the dienophile comprises an α,β–unsaturated carbonyl compound.

79. The invention of claim 77 wherein the dienophile comprises an α,β–unsaturated aldehyde.

80. The invention of claim 70 wherein the hydrogen bonding solvent comprises a solvent selected from the group consisting of chloroform, *t*-butanol, *i*-propanol, 2-butanol, and combinations thereof.

81. The invention of claim 70 wherein the hydrogen bonding solvent comprises 2-butanol.

82. The invention of claim 70 wherein the first reactant is selected from the group consisting of a 1-dialkylamino-3-siloxy diene and a 1-dialkylamino diene, and wherein the second reactant is selected from the group consisting of a ketone and an α,β–unsaturated carbonyl compound.

83. The invention of claim 70 wherein the first reactant comprises a 1-dialkylamino-3-siloxy diene and the second reactant comprises a cyclic ketone.

84. The invention of claim 70 wherein the first reactant is selected from the group consisting of a 1-dialkylamino-3-siloxy diene and a 1-dialkylamino diene and the second reactant comprises an α,β–unsaturated aldehyde group.

85. The invention of claim 73 wherein the heterodienophile comprises an unsaturated moiety having a structure represented by X=Y, wherein:

X is selected from the group consisting of $R^1{}_2C$, R^2N, O, and S; and

Y is selected from the group consisting of O, NR^2 , and S;

wherein R^1 is selected from the group consisting of hydrogen, halogen, alkyl, alkene, alkyne, cycloalkyl, aryl, heteroatom containing alkyl, and heteroatom containing aryl; and

wherein R^2 is selected from the group consisting of hydrogen, halogen, alkyl, alkene, alkyne, cycloalkyl, aryl, heteroatom containing alkyl, heteroatom containing cycloalkyl, and heteroatom containing aryl.

86. The invention of claim 73 wherein the heterodienophile comprises a moiety selected from the group consisting of aldehydes, ketones, esters, amides, carbonates, thioaldehydes, thioamides, thiocarbonates, lactones, lactams, thiolactones, thiolactams, imines, oximes, hydrazones, thionoesters, thioesters, dithioesters, thionolactones, dithiolactones, phosphorus ylides, thioketones, acid halides, anhydrides, iminium ions, nitroso-containing compounds, nitro-containing compounds, compounds containing a phosphorus-oxygen π-bond, and compounds containing a phosphorus-sulfur π -bond.

87. A reaction mixture comprising:

a diene;

a dienophile; and

a hydrogen bonding solvent.

88. The invention of claim 87 wherein the reaction mixture is substantially free of metals.

89. The invention of claim 87 wherein the dienophile comprises a heterodienophile.

90. The invention of claim 89 wherein the heterodienophile comprises a ketone.

91. The invention of claim 90 wherein the ketone comprises a cyclic ketone.

92. The invention of claim 87 wherein the dienophile comprises an α,β–unsaturated carbonyl compound.

93. The invention of claim 87 wherein the dienophile comprises an α,β–unsaturated aldehyde.

94. The invention of claim 87 wherein the hydrogen bonding solvent comprises a solvent selected from the group consisting of chloroform, *t*-butanol, *i*-propanol, 2-butanol, and combinations thereof.

95. The invention of claim 87 wherein the hydrogen bonding solvent comprises 2-butanol.

96. A method of performing an asymmetric catalytic reaction comprising:

combining a first reactant, a second reactant, and a catalytic amount of a chiral hydrogen-bond donor in a solvent to form a reaction mixture; and

reacting the first reactant and the second reactant to form an enantiomeric excess of a reaction product.

97. The invention of claim 96 wherein the reaction comprises a [4+2] cycloaddition.

98. The invention of claim 96 wherein the reaction mixture is substantially free of metals.

99. The invention of claim 97 wherein the first reactant comprises a diene and the second reactant comprises a heterodienophile.

100. The invention of claim 99 wherein the heterodienophile comprises a carbonyl group.

101. The invention of claim 99 wherein the heterodienophile comprises an aldehyde.

102. The invention of claim 99 wherein the heterodienophile comprises an ketone.

103. The invention of claim 99 wherein the heterodienophile comprises an α,β–unsaturated carbonyl compound.

104. The invention of claim 99 wherein the heterodienophile comprises an α,β–unsaturated aldehyde.

105. The invention of claim 96 wherein the chiral hydrogen-bond donor comprises a chiral alcohol.

106. The invention of claim 105 wherein the chiral alcohol comprises a 1,3-diol group.

107. The invention of claim 105 wherein the chiral alcohol comprises a 1,4-diol group.

108. The invention of claim 105 wherein the chiral alcohol comprises a 1,6-diol group.

109. The invention of claim 105 wherein the chiral alcohol comprises a TADDOL skeleton.

110. The invention of claim 105 wherein the chiral alcohol is selected from the group consisting of TADDOL, 1-Napthyl-TADDOL, 2-Napthyl-TADDOL, TADDOL derivatives, BINOL, BINOL derivatives, tartaric acid dialkyl ester derivatives, and hydrobenzoin derivatives.

111. The invention of claim 96 wherein the enantiomeric excess is at least 60 %.

112. The invention of claim 96 wherein the enantiomeric excess is at least 70 %.

113. The invention of claim 96 wherein the enantiomeric excess is at least 80 %.

114. The invention of claim 96 wherein the enantiomeric excess is at least 90 %.

115. The invention of claim 96 wherein the enantiomeric excess is at least 95 %.

116. The invention of claim 97 wherein the first reactant comprises an alkyne and the second reactant comprises an aldehyde.

117. The invention of claim 116 further comprising adding an organometallic reagent to the reaction mixture.

118. The invention of claim 117 wherein the organometallic reagent is diethyl zinc.

119. A reaction mixture comprising:

a first reactant selected from the group consisting of diene and an alkyne;

a second reactant selected from the group consisting of a dienophile and an aldehyde, wherein the second reactant is complementary in reactivity to the first reactant;

a solvent; and

a catalytic amount of a chiral hydrogen-bond donor.

120. The invention of claim 119 wherein the reaction mixture is substantially free of metals.

121. The invention of claim 119 wherein the first reactant comprises a diene and the second reactant comprises a dienophile.

122. The invention of claim 121 wherein the dienophile comprises a heterodienophile.

123. The invention of claim 122 wherein the heterodienophile comprises a carbonyl group.

124. The invention of claim 122 wherein the heterodienophile comprises an aldehyde.

125. The invention of claim 122 wherein the heterodienophile comprises an α,β–unsaturated aldehyde.

126. The invention of claim 119 wherein the first reactant comprises an alkyne and the second reactant comprises an aldehyde.

127. The invention of claim 126 wherein the reaction mixture further comprises an organometallic reagent.

128. The invention of claim 127 wherein the organometallic reagent comprises diethylzinc.

129. The invention of claim 119 wherein the chiral hydrogen-bond donor comprises a chiral alcohol.

130. The invention of claim 129 wherein the chiral alcohol comprises a 1,3-diol group.

131. The invention of claim 129 wherein the chiral alcohol comprises a 1,4-diol group.

132. The invention of claim 129 wherein the chiral alcohol comprises a 1,6-diol group.

133. The invention of claim 129 wherein the chiral alcohol comprises a TADDOL skeleton.

134. The invention of claim 129 wherein the chiral alcohol is selected from the group consisting of TADDOL, 1-Napthyl-TADDOL, 2-Napthyl-TADDOL, TADDOL derivatives, BINOL, BINOL derivatives, tartaric acid dialkyl ester derivatives, and hydrobenzoin derivatives.

135. In a method of performing a hetero-Diels-Alder reaction that includes reacting a diene with a heterodienophile, the improvement comprising performing the reaction in a hydrogen bonding solvent selected from the group consisting of chloroform, *t*-butanol, *i*-propanol, 2-butanol, and combinations thereof.